

55/cw/11/25

1999 NASA/ASEE SUMMER FACULTY FELLOWSHIP PROGRAM

**JOHN F. KENNEDY SPACE CENTER
UNIVERSITY OF CENTRAL FLORIDA**

**CHARACTERIZATION OF MOLYBDATE CONVERSION COATINGS FOR
ALUMINUM ALLOYS BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY**

Luz Marina Calle
Professor
Chemistry Department
Randolph-Macon Woman's College
NASA Colleague: Louis G. MacDowell

ABSTRACT

Electrochemical impedance spectroscopy (EIS) was used to investigate the corrosion inhibiting properties of newly developed proprietary molybdate conversion coatings on aluminum alloy 2024-T3 under immersion in aerated 5% (w/w) NaCl. Corrosion potential and EIS measurements were gathered for six formulations of the coating at several immersion times for two weeks. Nyquist as well as Bode plots of the data were obtained. The conversion-coated alloy panels showed an increase in the corrosion potential during the first 24 hours of immersion that later subsided and approached a steady value. Corrosion potential measurements indicated that formulations A, D, and F exhibit a protective effect on aluminum 2024-T3. The EIS spectra of the conversion-coated alloy were characterized by an impedance that is higher than the impedance of the bare alloy at all the immersion times. The low frequency impedance, Z_{lf} (determined from the value at 0.05 Hz) for the conversion-coated alloy was higher at all the immersion times than that of the bare panel. This indicates improvement of corrosion resistance with addition of the molybdate conversion coating. Scanning electron microscopy (SEM) revealed the presence of cracks in the coating and the presence of cubic crystals believed to be calcium carbonate. Energy dispersive spectroscopy (EDS) of the test panels revealed the presence of high levels of aluminum, oxygen, and calcium but did not detect the presence of molybdenum on the test panels. X-ray photoelectron spectroscopy (XPS) indicated the presence of less than 0.01 atomic percent molybdenum on the surface of the coating.

ACKNOWLEDGEMENT

I would like to express my deepest appreciation to Louis MacDowell of the Materials Science Division and to NASA/ASEE for providing me with the opportunity to participate in the 1999 Summer Faculty Fellowship Program. My professional development and my appreciation for the space program have been enhanced considerably during the ten weeks of the fellowship. Gregg Buckingham, Dr. E. Ramon Hosler, Dr. Jane Hodges, and Ms. Judie Gilliam provided the leadership and support that makes this program such a rich and wonderful experience for the faculty fellows. Jane, with her enthusiasm and interest in the program, provided us with unique opportunities to learn about NASA and the Kennedy Space Center. Ray and Judie were always there for us when we needed them.

I would also like to acknowledge Claudia Amorim, a student intern from Brazil, for performing the EIS measurements. Her professionalism and enthusiasm were an asset to this project. Scott Murray, Jennie Cummings, Peter Marciniak, Patrick Faughnan, Steve McDanel, and Don Parker in the Materials Engineering Section of the Materials Science Division were always there to help and provided me with a warm and friendly environment during long hours of research. Peter contributed with his photographic skills to the project. Jennie contributed her expertise in SEM and EDS. Stan Young of the Analytical Chemistry section also performed SEM and EDS on the exposed areas of the test panels. Dr. Mike Hampton of the University of Central Florida performed the XPS analysis.

CHARACTERIZATION OF MOLYBDATE CONVERSION COATINGS FOR ALUMINUM ALLOYS BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Luz Marina Calle

1. INTRODUCTION

Chromate conversion coatings have been used for the protection of aluminum alloys for over 70 years. Although their efficiency in minimizing corrosion attack is excellent, there are health and safety concerns over their use due to their toxicity and carcinogenic nature. Despite an extensive research effort over the past decade, a completely satisfactory replacement for chromate conversions coatings has yet to be identified.

Hexavalent molybdenum has received attention recently as a replacement for chromate conversion coatings. Molybdate mimics chromate in a variety of applications but it exhibits significantly lower toxicity.¹ Several proprietary molybdate conversion coatings have been developed for NASA. Six proprietary formulations of the coatings on aluminum alloy 2024-T3 were available for characterization by Electrochemical Impedance Spectroscopy (EIS).

2. EXPERIMENTAL PROCEDURE

Test Samples

Six proprietary formulations (labeled A-F) were provided by Lynntech, Inc. (College Station, Texas). Panels of aluminum 2024-T3 alloy (with average composition of 4.4% Cu, 0.6% Mn, 1.5% Mg, and 93.5%) were cut to a size of 10.16 cm × 15.24 cm (4" × 6") and treated with a formulation of the molybdenum conversion coating.

Corrosion Potential Measurements

Corrosion potential measurements were performed using a system manufactured by EG&G Princeton Applied Research Corporation. The system used includes: (1) the Model 273 Computer-Controlled Potentiostat/Galvanostat, (2) the Model 5210 Computer-Controlled Lock-In Amplifier, and (3) the Model 352 SoftCorr™ III Corrosion Measurement Software. The electrochemical cell included a saturated Calomel electrode, SCE, a platinum counter electrode, the sample working electrode, and a bubbler/vent tube. Three electrochemical cells were used. The flat specimen holders exposed a surface area of 1 cm², 13 cm², or 32 cm² depending on the cell that was used. Corrosion potential values were gathered for one hour in aerated 5% (w/w) NaCl before the first set of EIS measurements was obtained. Subsequent corrosion potential values were collected before each set of EIS measurements which were collected at several time intervals up to a maximum of 168 hours. All solutions were prepared using deionized water.

Electrochemical Impedance Measurements

A Model 378 Electrochemical Impedance system manufactured by EG&G Princeton Applied Research Corporation was used for all EIS measurements. The system includes: (1) the Model 273 Computer-Controlled Potentiostat/Galvanostat, (2) the Model 5210 Computer-Controlled Lock-In Amplifier, and (3) the Power Sine Electrochemical Impedance Software. Data were gathered in the frequency range from 100 kHz to 0.01 Hz. The AC amplitude used for the experiments was 10 mV. Each sample was studied at various immersion times in aerated 5% (w/w) NaCl for up to one week.

Bode magnitude plots of the data (showing the logarithm of the modulus of the impedance, $\log |Z|$, as a function of the logarithm of frequency and phase angle, α in degrees, as a function of the logarithm of frequency) as well as Nyquist plots (showing the negative of the imaginary component of impedance as a function of the real component of the impedance) were obtained for each formulation.

Scanning Electron Microscopy (SEM)/Energy Dispersive Spectroscopy (EDS)

SEM examinations were carried out on a JEOL JSM-6100 scanning electron microscope at 5.0 to 25.0 kV. Phase identification was done using EDS in SEM with a Kevex SI(LI) detector.

X-ray Photoelectron Spectroscopy (XPS)

Samples were analyzed with a Kratos XSAM800 X-ray photoelectron spectrometer with argon etching between analyses (for a total of 40 minutes).

3. RESULTS AND DISCUSSION

Corrosion Potential Measurements

Corrosion potential values gathered during the hour immediately preceding the first set of EIS measurements for each molybdate formulation indicated that an hour was sufficient to allow the potential to equilibrate. Subsequent values of the corrosion potential were obtained immediately before each set of EIS measurements was collected. Figure 1 shows the change in corrosion potential with immersion time for all formulations of the molybdate conversion-coated panels and for a bare aluminum alloy panel. The coated panels showed a steady increase in the corrosion potential towards the corrosion potential of the aluminum alloy during the first 24 hours of immersion. A gradual increase in corrosion potential with immersion time is expected if the coating encourages slow but uniform (i.e., pit free) growth of the oxide layer. This behavior was observed for all formulations. The initial increase in the corrosion potential subsided and after 48 hours of immersion a steady value of the corrosion potential was obtained. Panels coated with formulations A, D, and F achieved a corrosion potential slightly higher than the corrosion potential of the aluminum alloy while panels B, C, and E achieved a corrosion

potential that was lower. A shift of the corrosion potential of the alloy in the positive direction is indicative of the presence of a protective effect on the aluminum alloy. Visual inspection of the panels revealed that panels A,D, and F had the fewest number of corrosion spots per cm².

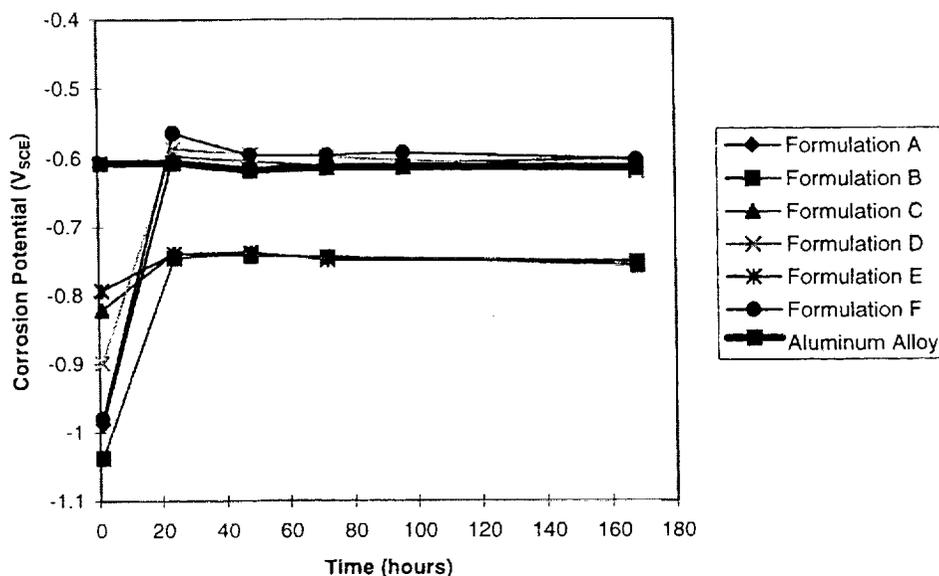


Figure 1. Corrosion potential as a function of immersion time in 5% (w/w) NaCl

Electrochemical Impedance Spectra

Figure 2 shows representative impedance spectra (Bode format: The phase angles have been omitted for clarity) for formulation A and for aluminum 2024-T3 at various immersion times. The impedance of the coated alloy is greater than the impedance of the bare alloy at all frequencies. The higher value of the impedance is indicative of the improvement of corrosion resistance with the addition of the molybdate conversion coating.

The low-frequency impedance, Z_{lf} (determined from data at 0.05 Hz), has been proposed as the optimal EIS parameter to evaluate the performance of corrosion inhibiting coatings on aluminum.² The impedance at this frequency includes the response of the coating as well as part of the response of the oxide and/or corrosion product in the pores at the metal interface. Z_{lf} reflects the condition of the substrate as well as that of the coating. Although the Z_{lf} values do not give information about how a coating degrades (i.e., water uptake, blistering, etc.), they correlate with coating performance. Figure 3 shows the variation of Z_{lf} with immersion time for the molybdate-coated as well as the bare aluminum alloy. Z_{lf} values for the molybdate coated

panels are in the order of 10^3 - $10^5 \Omega\text{cm}^2$ while those for the bare panel are of the order of $10^3 \Omega\text{cm}^2$. Low frequency impedance for chromate conversion coatings on aluminum alloy 2024 after 3 hours of immersion in aerated 0.5 M (3%) NaCl have been reported³ as being in the order of $10^4 \Omega\text{cm}^2$. This value is lower than $10^{10} \Omega\text{cm}^2$ which is the value expected of an excellent barrier coating.⁴

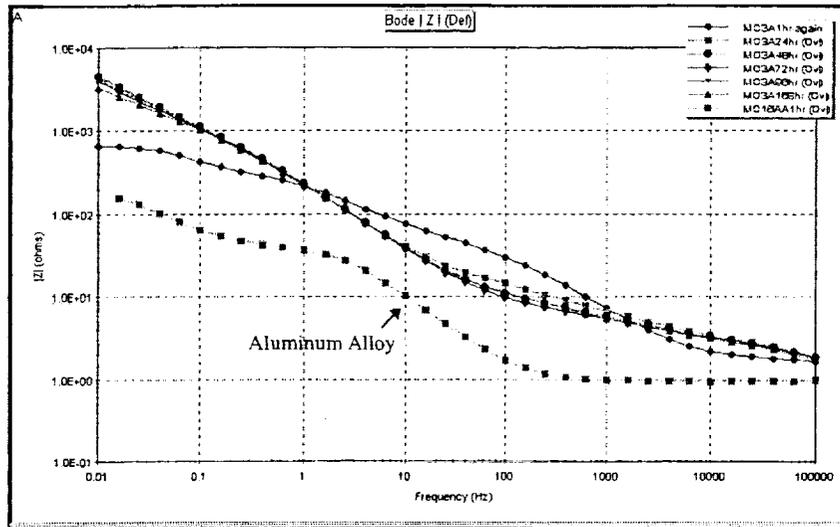


Figure 2. Bode plots for formulation A and aluminum alloy at different immersion times

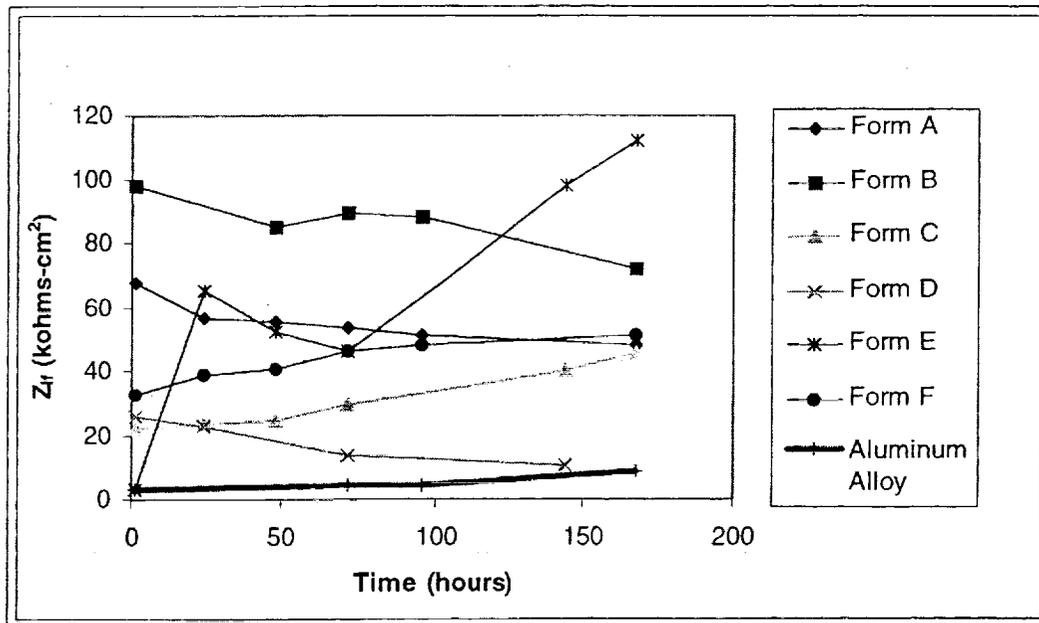


Figure 3. Low frequency impedance Z_{lf} as a function of immersion time in NaCl 5% (w/w) NaCl

Impedance data in the Nyquist format were analyzed using the simplified equivalent circuit shown in Figure 4. This circuit gives a coating resistance (R_c) which can be used as a figure of

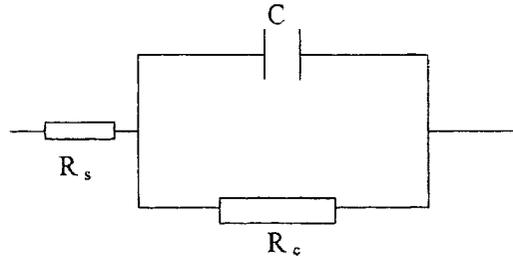


Figure 4. Simplified circuit for conversion-coated aluminum alloys⁵

merit to assess coating performance. Values for R_c for each conversion-coated and for the bare panel are shown in Figure 5. The conversion-coated panels achieved R_c values in the 10^4 - 10^5 Ωcm^2 range while the bare aluminum alloy panel had R_c values in the order of 10^3 Ωcm^2 .

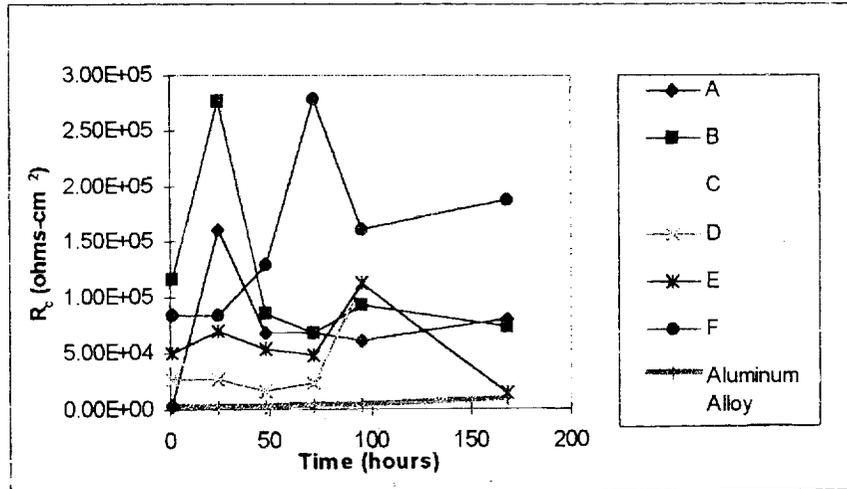


Figure 5. Apparent integrated resistance as a function of immersion time

The threshold R_c value⁵ proposed to define the minimum value for which a given coating can be expected to attain a passing result in a 168-hour salt spray test for aluminum 2024-T3 is 2×10^6 Ωcm^2 to 5×10^6 Ωcm^2 . None of the conversion-coated panels attained these values despite their successful performance in salt fog testing. However, the reliability of salt spray results as well as the use of EIS data for prediction of salt spray performance has been challenged by Mansfeld.⁶

SEM/EDS

SEM of the of one of the conversion coated panels (formulation A) revealed the presence of cracks on the coating as well as the presence of cubic crystals (see Figure 6). EDS analysis of the crystals indicated the presence of high concentrations of calcium as well as oxygen (see Figure 7).

This information can be interpreted as evidence of the presence of calcium carbonate on the coating.

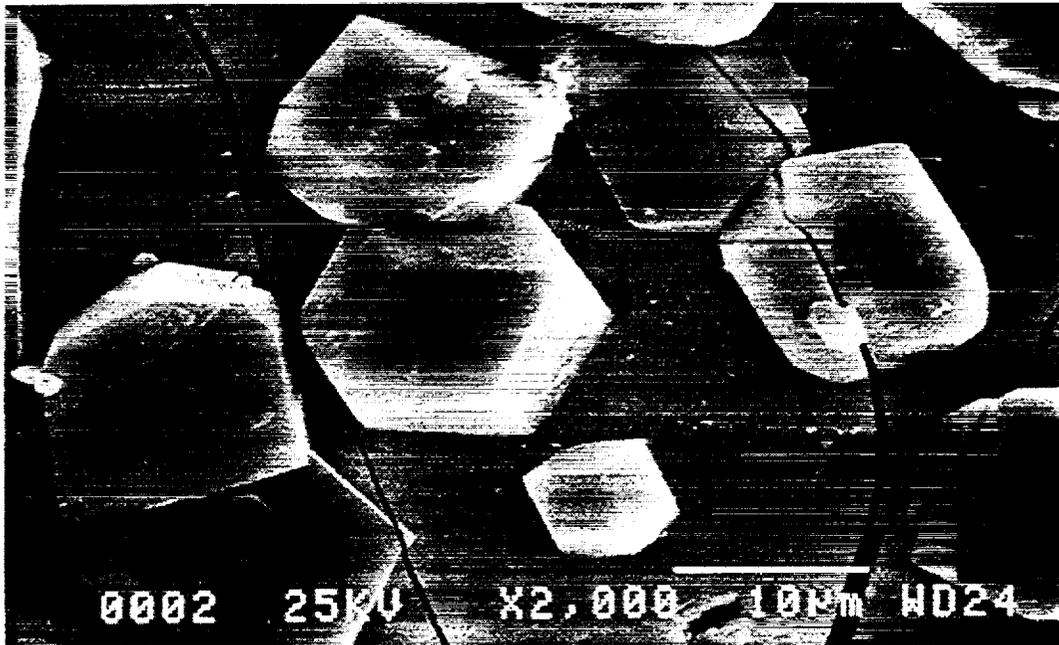


Figure 6. SEM micrograph of conversion-coated (formulation A) aluminum alloy

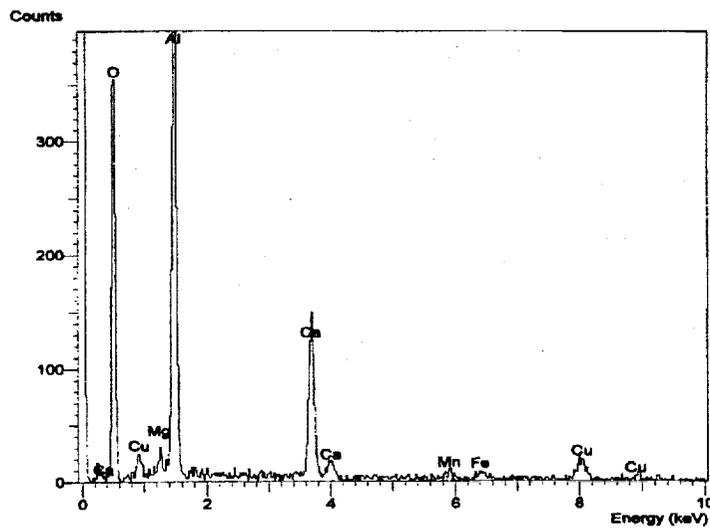


Figure 7. EDS spectrum of conversion-coated (formulation A) aluminum alloy

EDS analysis did not detect the presence of molybdenum in the coating. This finding can be attributed to the fact that EDS is sensitive to most elements if they are present above 0.4% by weight.

XPS

The conversion-coating was further analyzed by x-ray photoelectron spectroscopy (XPS) with argon etching between analyses. The sample showed a small peak in the XPS spectrum that corresponded with the expected location of a molybdenum peak. This would amount to less than 0.01 atomic percent molybdenum on the surface of the sample.

4. CONCLUSIONS

Corrosion potential measurements indicated that formulations A, D, and F exhibit a protective effect on aluminum 2024-T3.

EIS results for the six formulations tested showed that there is an improvement in the corrosion resistance of aluminum 2024-T3 with the addition of the molybdate conversion coating.

SEM/EDS revealed the presence of cracks in the coating. Cubic crystals of what it is believed to be calcium carbonate were also observed on the surface of the coating. SEM/EDS failed to detect the presence of molybdenum in the coating.

XPS analysis of the coating indicated that there is less than 0.01 atomic percent molybdenum on the surface of the sample.

Further analysis of the EIS data as well as data gathered from atmospheric exposure of the panels are suggested before more definite conclusions can be drawn.

REFERENCES

-
- [1] B.A. Shaw, G.D. Davis, T.L. Fritz, and K.A. Oliver, *J. electrochem. Soc.*, 137 (1990): p. 359.
 - [2] J.A. Grandle and R.S. Taylor, *Corrosion*, 50 (1994): p. 792.
 - [3] J.E.O. Mayne, and D.J. Mills, *J. Oil & Colour Chemists Assoc.*, 58 (1975) p. 155.
 - [4] R. G. Buchheit, M.D. Bode, and G.E. Stoner, *Corrosion*, 50 (1994): p. 205.
 - [5] R.G. Buchheit, M. Cunningham, H. Jensen, M.W. Kendig, and M.A. Martinez, *Corrosion*, 54 (1998): p. 61.
 - [6] F. Mansfeld, *Corrosion*, 54 (1998): p. 595.

